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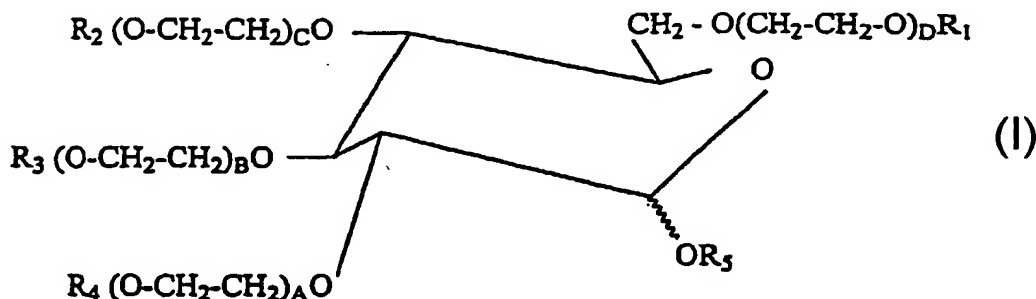
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(54) Title: FATTY ACID ESTERS OF ETHOXYLATED ALKYLGLUCOSIDES



(57) Abstract: A mixture of fatty acid esters of ethoxylated alkylglucosides of formula I is useful as a refatting agent in cosmetic formulations. Formule (I). Wherein the sum of A, B, C and D is from 10 to 60, each R₁, R₂, R₃ and R₄ independently is hydrogen or -C(o)-M, wherein M is a C₁₁-C₂₉ alkyl or alkenyl, and R₅ is a C₁-C₅ alkyl, provided that the ethoxylated alkylglucoside on the average comprises from 2.1 to 2.8 -C(o)-M groups.

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FATTY ACID ESTERS OF ETHOXYLATED ALKYLGLUCOSIDES

The present invention relates to a mixture of fatty acid esters of ethoxylated
5 alkylglucosides and their use in cosmetic compositions.

Glucose derivatives, such as fatty acid esters of alkoxyated alkylglucosides, may be
produced from renewable raw materials. Due to agricultural over-production the starting
materials are low in cost and available in unlimited amounts. Therefore, much research
10 efforts have been spent on the development of ethoxylated alkylglucosides and their uses.

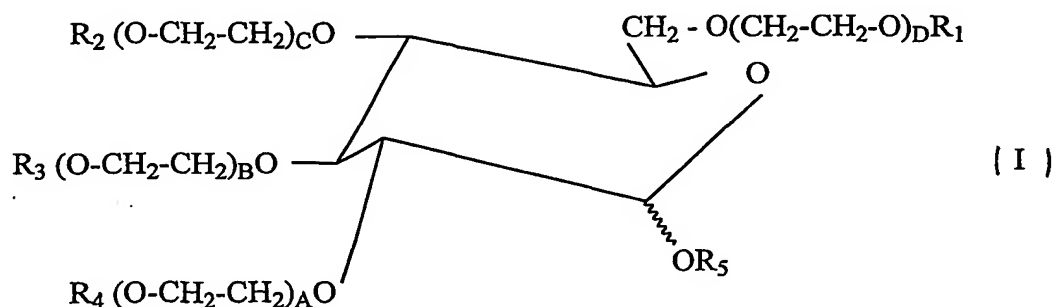
US Patent No. 4,364,930 discloses a stable oil-in-water emulsion for use in cosmetic
or pharmaceutical compositions. The emulsifying system comprises among other
components a mixture of (1) mono- and/or dialkyl carboxylates of alpha-methyl glucoside
15 and (2) mono- and/or dialkyl carboxylates of alpha-methyl glucoside which has been
polyoxyethylenated with 10-30 moles of ethylene oxide.

US Patent No. 5,502,175 discloses fatty acid esters which are prepared by
ethoxylating methylglucoside with from 84 to 300 moles, preferably 120 moles of ethylene
20 oxide and subsequent esterification with 2-4 moles, preferably 1.8-3.5 moles of a saturated
or unsaturated C₁₁-C₁₈ fatty acid. The prepared fatty acids are used in shampoos and foam
baths. They act as a thickening agent and have a good moisturizing effect and reduce
irritation values of common ingredients, such as anionic and non-ionic surfactants.

25 U.S. Patent No. 4,687,843 discloses esterified propoxylated methyl glucoside
compositions which are useful as skin moisturizers and emollients.

One object of the present invention is to find new acid esters of alkoxyated
alkylglucosides. Another object of the present invention is to find acid esters of alkoxyated
30 alkylglucosides which are useful in skin conditioning, and in particular as an enhancer of
skin lipids, that means as a refatting agent.

One aspect of the present invention is a mixture of fatty acid esters of an ethoxylated alkylglucoside of formula I



wherein the sum of A, B, C and D is from 10 to 60, each R_1 , R_2 , R_3 and R_4 independently is hydrogen or $-C(O)-M$, wherein M is a $C_{11}-C_{29}$ alkyl or alkenyl, and R_5 is a C_1-C_5 alkyl, provided that the ethoxylated alkylglucoside on the average comprises from 2.1 to 2.8 $-C(O)-M$ groups.

Another aspect of the present invention is a cosmetic composition which comprises the mixture of fatty acid esters.

Yet another aspect of the present invention is the use of the mixture of fatty acid esters as a refatting agent in a cosmetic composition.

Yet another aspect of the present invention is a process for preparing the mixture of fatty acid esters, which process comprises the steps of

i) reacting an alkylglucoside with from 10 to 60 moles of ethylene oxide per mole of

alkylglucoside and

ii) reacting the ethoxylated alkylglucoside with from 2.1 to 2.8 moles of a saturated or unsaturated $C_{11}-C_{29}$ fatty acid or a C_{1-4} -alkyl ester thereof.

The fatty acid esters of the ethoxylated alkylglucosides of the present invention are a mixture of molecules with different degrees of esterification such that the compounds of formula I on the average comprise from 2.1 to 2.8, preferably from 2.2 to 2.7, more preferably from 2.3 to 2.5, most preferably about 2.4 $-C(O)-M$ groups.

Generally the degree of ethoxylation of the individual molecules also varies somewhat, as it is typical for oligomers. However, the average degree of ethoxylation, that means the sum of A, B, C and D is from 10 to 60, preferably from 25 to 50, more preferably from 30 to 40, most preferably about 35. A, B, C and D each independently can have the meaning of from 0 to 60, provided that the sum of A, B, C and D is from 10 to 60.

In formula I M is $C_{11} - C_{29}$ alkyl or alkenyl, preferably $C_{11} - C_{19}$ alkyl or alkenyl, more preferably $C_{16} - C_{18}$ alkenyl, most preferably a C_{17} alkenyl group. The alkyl and alkenyl group may be branched, but preferably it is straight.

In formula I R_5 is an alkyl group of from 1 to 5 carbon atoms, preferably from 1 to 3 carbon atoms, most preferably methyl.

The fatty acid esters of the present invention can be prepared by preparing first a mixture of fatty acid esters of an alkylglucoside and then ethoxylating the product. However, according to a preferred process the fatty acid esters are prepared by ethoxylating an alkylglucoside and subsequent esterification.

The ethoxylation can be accomplished in one, two or more steps. The reaction temperature generally is from 100 to 190°C, preferably from 130 to 160°C, more preferably from 145 to 155°C. The reaction pressure generally is from 100 to 1000 kPa, preferably from 200 to 600 kPa, more preferably from 250 to 550 kPa.

When carrying out the ethoxylation step in one step, an alkylglucoside, preferably methylglucoside, is ethoxylated with from 10 to 60, preferably from 25 to 50, more preferably from 30 to 40, most preferably with about 35 moles of ethylene oxide per mole of the alkylglucoside. Generally a basic catalyst is used, preferably an alkali metal hydroxide, more preferably potassium or sodium hydroxide. The amount of catalyst generally is from 0.2 to 5 weight-percent, preferably from 0.5 to 2.5 weight-percent, based on dry alkylglucoside. The ethoxylation is generally conducted under an inert atmosphere using a gas like argon, helium, or preferably nitrogen. The ethoxylation is generally completed within 2 to 6 hours.

In an alternate embodiment of the present invention the ethoxylation is accomplished in two steps. An ethoxylated alkylglucoside which preferably comprises from 5 to 25 moles, more preferably from 10 to 20 moles, most preferably about 20 moles of groups derived from ethylene oxide per mole of alkylglucoside, is used as starting material for further ethoxylation. The preferred starting materials are commercially available from Amerchol Corp. under the trademark Glucam E-10 or Glucam E-20. The ethoxylated alkylglucoside is converted to the corresponding alkoxide salt by reacting the ethoxylated alkylglucoside with a base, preferably an alkali metal hydroxide, most preferably with potassium or sodium hydroxide. The alkali metal hydroxide is preferably used as a 0.1 to 1 weight percent, more preferably 0.25 to 0.5 weight percent, aqueous solution. The ethoxylation is carried out as described above with a corresponding smaller amount of ethylene oxide.

The subsequent esterification is effected by direct esterification with from 2.1 to 2.8, preferably from 2.2 to 2.7, more preferably from 2.3 to 2.5, most preferably about 2.4 moles of a fatty acid or by transesterification with a corresponding amount of a fatty acid ester.

The fatty acid used for direct esterification is a saturated or unsaturated $C_{11} - C_{29}$ fatty acid, preferably a $C_{11} - C_{19}$ fatty acid, more preferably a $C_{16} - C_{18}$ fatty acid or a blend of such fatty acids. Preferred fatty acids are stearic acid, linoleic acid, linolenic acid, lauric acid, palmitic acid, undecanoic acid, or most preferably oleic acid. The direct esterification with a saturated or unsaturated $C_{11} - C_{29}$ fatty acid can be carried out according to a process known in the art, for example by an acid catalyzed reaction.

For transesterification C_{1-4} -alkyl esters of the mentioned $C_{11} - C_{29}$ fatty acids are preferred, more preferably the methyl esters of the mentioned $C_{11} - C_{29}$ fatty acids. Methyl oleate is the most preferred fatty acid ester. The transesterification is generally conducted in the presence of a base catalyst. The catalyst is preferably an alkali metal hydroxide, such as potassium or sodium hydroxide. Generally from 0.03 to 1 weight percent, preferably from 0.1 to 0.5 weight percent of base catalyst is used, based on the weight of ethoxylated alkylglucoside. The reaction temperature generally is from 130 to 200 °C, preferably from 160 to 185°C, more preferably from 170 to 180°C. The reaction is preferably conducted

under vacuum. More preferably, the vacuum starts at about 125 mm Hg and ends at about 3 mm Hg. The reaction typically takes 4 to 6 hours.

The above-described mixture of fatty acid esters is useful in cosmetic compositions, particularly in skin cleansing compositions. Cleansing the skin does not only remove dirt but also removes fats and oils, which leaves the skin feeling dry and taut. Therefore, the cosmetic industry spends much research effort to find conditioning agents which are useful in skin cleansing compositions. This presents a major challenge, since a refatting agent should fulfill a variety of requirements. It should enhance skin lipids by leaving the skin smoother, less dry, and a causing a positive tactile sensation. It should not unduly increase the viscosity of the cleansing composition, otherwise the cleansing composition is not pourable and not accepted by the consumers. Also, the refatting agent should not provide an unpleasant odor or color to the cleansing composition. It should not adversely affect clarity or foaming and be compatible with other cleansing ingredients.

It has surprisingly been found that the above-described mixture of fatty acid esters of ethoxylated alkylglucosides is useful as a refatting agent in cosmetic formulations, such as skin cleansing compositions. The mixture of fatty acid esters is generally a clear or slightly hazy liquid with a viscosity low enough to be pourable. It has generally a light yellow color.

The cosmetic composition of the present invention generally comprises from 0.1 to 10, preferably from 0.5 to 5, more preferably from 1 to 3 weight percent of the mixture of fatty acid esters, based on the total weight of the cosmetic composition. Cosmetic compositions comprising the preferred fatty acid esters of the present invention have shown favorable results in sensory assessments wherein after-feel in skin washing tests are evaluated. It has also been found that the mixture of fatty acid esters does not adversely affect the foaming of cleansing formulation, but produces a creamier foam.

The cosmetic composition of the present invention may comprise a number of additives known in the art, such as water, surfactants, thickeners, conditioning agents, humectants, preservatives, perfumes, and colorants.

The present invention is further illustrated by the following examples which should not be construed to limit the scope of the present invention. All parts and percentages are by weight unless otherwise indicated.

5 Example 1

 A 1.5 liter glass pressure reactor, equipped to automatically feed ethylene oxide based on pressure, was charged with 589 g of ethoxylated methylglucoside (comprising 20 moles of ethylene oxide units per mole of methylglucoside) which contained about 0.25 weight percent potassium hydroxide. The contents of the reactor were heated and the reactor was evacuated
10 when the temperature of the contents reached about 130°C. Heating was continued. When the temperature of the reactor contents reached about 145°C, the reactor was pressurized with nitrogen to about 450 kPa (about 50 psig). The pressure was released to about 180 kPa (about 10 psig). This nitrogen pressurizing and releasing was repeated twice more. The reactor was then pressurized to about 275 kPa (about 23 psig). When the temperature of the contents
15 reached 155°C, ethylene oxide was fed into the reactor. The ethylene oxide feed rate was controlled so that the reactor pressure never exceeded about 550 kPa (about 65 psig). After about 376 g of ethylene oxide has been fed to the reactor, the ethylene oxide feed was stopped and the reactor was held at 155°C for 30 minutes to essentially react any remaining ethylene oxide. The reaction was cooled and the contents discharged to yield about 965 g of recovered
20 ethoxylated alkylglucoside comprising about 35 units derived from ethylene oxide per unit of alkylglucoside. The product was designated as E-35.

 For esterification of the ethoxylated alkylglucoside a laboratory round bottom glass reactor was charged with 100 grams of E-35 as prepared above, 41 g of methyl oleate, and 0.1
25 g of hypophosphorous acid. A nitrogen sparge was initiated and the contents of the reactor were heated to 175°C while applying vacuum. The vacuum was about 125 torrs. The reaction was held at 175°C with this vacuum for 30-60 minutes. The vacuum was then slowly increased to maximum, about 3 torrs and the reaction held under these conditions for 4 to 5 hours. The reaction mixture was cooled. Once its temperature was below 80°C, it was
30 neutralized with about 0.4 g of 88 percent aqueous lactic acid. The reactor contents were discharged and about 138 g of product were recovered. Based on weights charged, the product can be described as a mixture of fatty acid esters of ethoxylated methylglucoside comprising on

average 35 moles of groups derived from ethylene oxide and on average 2.4 moles of ester groups per mole of methyl glucoside.

The product was a slightly viscous, clear liquid and light yellow in color.

5

Example 2

Example 1 was repeated except that only about 37.6 grams of methyl oleate was used. The produced mixture of fatty acid esters of ethoxylated methyl glucoside comprised on average 35 moles of groups derived from ethylene oxide and on average 2.2 moles of ester groups per mole of methylglucoside.

10

Example 3

Example 1 was repeated except that 47.8 grams of methyl oleate was used. The produced mixture of fatty acid esters of ethoxylated methylglucoside comprised on average 35 moles of groups derived from ethylene oxide and on average 2.8 moles of ester groups per mole of methylglucoside.

15

The products of Examples 1-3 above was compared in a sensory test with PEG-7 Glycerol Cocoate (polyoxyethylene (7) glyceryl monococoate), which is commercially available as Cetiol HE (Trademark) from Cognis, and which is a leading refatting agent in the US market .

20

Formulation

A formulation consisting of 9 percent sodium laureth-2 sulfate, commercially available as Standapol ES-2 (Trademark) from Cognis; 4 percent cocamidopropyl betaine, commercially available as Velvetex BK-35 (Trademark) from Cognis, 1 percent decyl glucoside, commercially available as Plantaren 2000 (Trademark) from Cognis, and 85 percent water was prepared.

25

To produce the formulation from Examples 1-3, 1 percent of the product of Example 1, 2 or 3 was added to the Formulation.

30

Comparative Example A

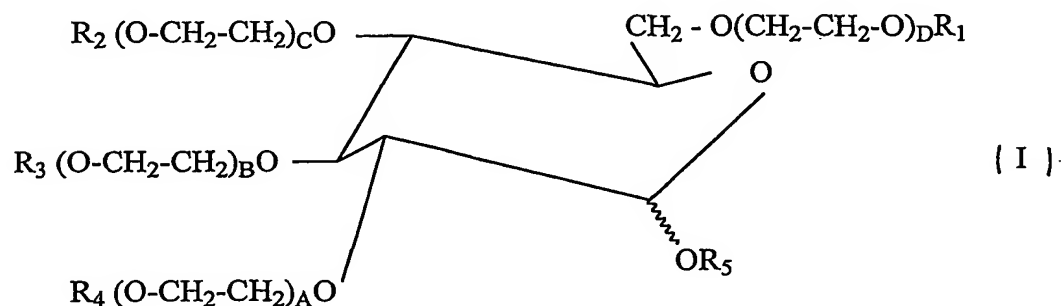
To produce the formulation of Comparative Example A, 1 percent of Cetiol HE (Trademark) was added to the Formulation.

- 5 A panel study of 20 people was conducted. Initially the panelist washed both hands with Ivory (Brand name) soap bar, and then placed a latex glove on one hand and washed the other hand with approximately one gram of either the formulation from one of the Examples 1-3 or with the formulation of Comparative Example A. The panelist noted the quality and quantity of foam and feel of the foam. The panelist then placed a glove on the other hand and repeated
- 10 the procedure with the other formulation, noting again the quality and quantity of the foam and feel of the foam. The panelist rinsed both hands, patted dry, and once fully dried, determined the feel of each hand with the other to determine any difference in after-feel. The percentage of people expressing a preference for the formulation of Example 1, 2 or 3 respectively over the formulation from Comparative Example A, the percentage of people expressing a preference
- 15 for the formulation from Comparative Example A and the percentage of people expressing no preference are listed in Table 1 below.

Example	Evaluation foam quantity and quality			After-feel sensory evaluation		
	Preference for invention	Preference for Comp. Ex. A	No preference	Preference for Comp. Ex. A	Preference for inventio	No preference
1	55	40	5	33	27	40
2	40	55	5	15	35	50
3	55	40	5	35	20	45

WHAT IS CLAIMED IS:

1. A mixture of fatty acid esters of an ethoxylated alkylglucoside of
 5 formula I



- wherein the sum of A, B, C and D is from 10 to 60, each R_1 , R_2 , R_3 and R_4
 10 independently is hydrogen or $-C(O)-M$, wherein M is a $C_{11}-C_{29}$ alkyl or alkenyl, and R_5
 is a C_1-C_5 alkyl, provided that the ethoxylated alkylglucoside on the average comprises
 from 2.1 to 2.8 $-C(O)-M$ groups.

2. The mixture of Claim 1 wherein the sum of A, B, C and D in formula
 15 I is from 25 to 50.

3. The mixture of Claim 2 wherein the sum of A, B, C and D in formula
 I is from 30 to 40.

- 20 4. The mixture of any one of Claims 1 to 3 wherein the ethoxylated
 alkylglucoside on the average comprises from 2.3 to 2.5 $-C(O)-M$ groups.

5. The mixture of any one of Claims 1 to 4 wherein M in formula I is a
 25 C_{17} alkenyl group.

6. The mixture of any one of Claims 1 to 5 wherein R_5 is methyl.

7. A cosmetic composition comprising the mixture of fatty acid esters of any one of Claims 1 to 6.

8. The cosmetic composition of Claim 7 being a skin cleansing
5 composition.

9. Use of the mixture of fatty acid esters of any one of Claims 1 to 6 as a refatting agent in a cosmetic composition.

10 10. A process for preparing the mixture of any one of Claims 1 to 6 comprising the steps of

i) reacting an alkylglucoside with from 10 to 60 moles of ethylene oxide per mole of alkylglucoside and

15 ii) reacting the ethoxylated alkylglucoside with from 2.1 to 2.8 moles of a saturated or unsaturated $C_{11} - C_{29}$ fatty acid or a C_{1-4} -alkyl ester thereof.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/18720

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07H15/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 687 843 A (POLOVSKY STUART B ET AL) 18 August 1987 (1987-08-18) cited in the application the whole document	1-10
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

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